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## PATENT SPECIFICATION



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### COMPLETE SPECIFICATION

#### Improvements in and relating to the Production of Titanium Dioxide Pigments

(A communication from TITAN COMPANY INC., a Corporation organised under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, and having an office address at 111, Broadway, City, County and State of New York, United States of America.)  
I, WILLIAM JOHN TENNANT, a British Subject, of 111/112, Hatton Garden, London, E.C.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—  
This invention relates to the production of titanium dioxide pigments.  
Titanium dioxide may be prepared by the hydrolysis of a titanium salt solution, the precipitate being calcined to give titanium dioxide in a form suitable for pigment purposes. It is known that the calcined product may exist as the anatase modification which has a refractive index of 2.55 or as the rutile modification which has a refractive index of 2.71. Weiser and Milligan (J. Phys. Chem. 38, 513, 1934) have shown that the product obtained by the hydrolysis of a titanium sulphate solution exists as the anatase modification and that the product obtained by the hydrolysis of a titanium chloride solution exists as the rutile modification. In view of the higher refractive index of the rutile modification it would be desirable to hydrolyse titanium chloride solutions, but at the present day commercial production is confined almost entirely to the preparation of the anatase modification from sulphuric acid solutions owing to the difficulty met on a commercial scale in obtaining precipitated particles of suitable form for pigment purposes from the titanium chloride solutions. The main difficulty is the fine state of division of the precipitate from the chloride solutions. Such a precipitate is usually in a peptised or extremely finely divided condition, and is in consequence difficult to filter and impossible to wash free from impurities contained in the mother liquor. As a result the calcined

products have a poor colour and a very low hiding power which makes them unsuitable for use as a pigment.

A large amount of work has been carried out on the preparation of titanium dioxide pigments from titanium salt solutions, and particular attention has been paid to the possibilities of obtaining a product in suitable form from titanium chloride solutions. The result of the investigations has been a number of suggestions, some of which have been adopted in practice, either to add to the hydrolysis solution materials which will assist the hydrolysis and influence the nature of the precipitate, or to effect the hydrolysis in the presence of suspended insoluble materials which influence the nature of the precipitate. Amongst other suggestions Mellor "A comprehensive treatise on inorganic and theoretical chemistry", Volume VII, page 40, indicates that hydrolysis may be facilitated when a titanium chloride solution is used by adding sulphur acid. He does not give any details as to quantities nor any details as to the manner in which the hydrolysis is influenced.

British Patent Specification No. 308,725 describes the hydrolytic precipitation of titanium compounds from mineral acid titaniferous solutions by adding the solution to a hot aqueous bath, the characteristic feature of the process being the presence of a small proportion of an organic acid dissolved in the hydrolysis liquor. No specific limits are set for the quantity of organic acid which may be present, but it is stated that they may be employed in relatively small proportions. A fairly large proportion is, however, contemplated as the amount is compared with that required for a double decomposition reaction with the titanium content of the solution, it being stated that the amount used may be much less than that required for such a double decomposition. The specific Examples describe the addition of 0.19 mol. and of .137 mol. of oxalic acid per mol. of  $\text{TiO}_2$  in a sulphuric acid solution. The purpose of the addition is to prevent aggre-

gation and the process is described mainly in conjunction with hydrolysis from sulphuric acid solutions. As is described more fully hereafter, whilst the acids have a dispersing action when used in the proportions described in No. 308,725, when a very small quantity namely less than .1 mol. of acid per mol. of  $TiO_2$  in a titanium chloride solution is employed, the surprising effect is observed that an aggregation is obtained, the precipitated particles being of a size which makes them more suitable for pigment purposes.

British Patent Specification No. 274,072 describes a process in which an attempt is made to obtain the advantages arising both from the addition of a soluble substance to the hydrolysis solution and the suspension of an insoluble material in the solution. According to that specification a small quantity of sulphuric acid is added to a hydrochloric acid solution, or a small quantity of hydrochloric acid is added to a sulphuric acid solution, and pure silica or aluminium silicate or a mixture is suspended in the solution and then hydrolysis is effected by heating to boiling. No specific limits are set to the amount of acid which is added, but the specific Example describes the addition of .16 mol. of sulphuric acid per mol. of  $TiO_2$  in a hydrochloric acid solution. In this case the silica is employed owing to the physical action which it has on the degree of dispersion of the precipitate, this action has been recognised by others, for example it is described in British Patent Specification No. 309,051. The disadvantage of such a process is that composite pigments only may be obtained.

It is the object of the present invention to obtain by the hydrolytic precipitation of titanium chloride solutions, pure titanium dioxide which in addition to having the rutile crystalline structure has the other requisite pigment properties.

The process for the production of titanium dioxide having the rutile structure according to the present invention comprises hydrolysing an aqueous titanium tetrachloride solution and calcining the product and is characterised by effecting the hydrolytic precipitation in the presence of a negative divalent ion derived from a substance added to the solution in a proportion not exceeding 0.1 mol. to each mol. of titanium reckoned as  $TiO_2$  present in the hydrolysis solution, and by effecting the hydrolysis in the absence of any added insoluble material suspended in the hydrolysis solution.

The negative divalent ion has a catalytic action and this action is dependent on it being present in the limited quantity specified. When it is present in such a

quantity the resulting precipitate is not peptised and can be readily filtered and washed prior to calcination when a product having the rutile crystalline structure and other desirable pigment properties is obtained.

The process of the present invention involves relatively rapid precipitation in the presence of the negative divalent ion, and is preferably carried out by adding an aqueous solution of titanium tetrachloride to hot water containing a small amount of the negative divalent ion and then heating the mixed solutions to effect hydrolytic precipitation.

The negative divalent ion may be derived conveniently from sulphuric, tartaric or oxalic acid or one of their alkali metal salts, such as sodium sulphate  $Na_2SO_4$ , sodium oxalate  $Na_2C_2O_4$ , and sodium tartrate  $Na_2C_4H_2O_6$ . These acids dissociate in aqueous solution to give a divalent negative ion and at the same time are compatible with the strongly acid solution used.

The pigments obtained in accordance with the invention show a remarkably improved tinting strength and hiding power over titanium dioxide pigments which have normally been available hitherto on a commercial scale. Thus when the tinting strength is determined by the tentative method of test of the American Society of Testing Materials, A.S.T.M. Designation: D352-31T, A.S.T.M. Tentative Standards 1933, 525, the usual commercial products give about 1100-1200 as the highest value whilst the pigments of the present invention have given values of 1400-1500. The hiding power of the titanium dioxide pigment of the invention is likewise correspondingly greater than the hiding power of the usual commercial products, a fact which may be attributed to the rutile form of the pigment of the invention and its consequential higher refractive index than the anatase form of the usual products.

Another advantage of the process of the invention is the high state of purity of the products as in this respect they are superior to titanium dioxide pigments normally prepared by precipitation from sulphuric acid solutions.

The following specific Example illustrates the manner in which the process of the invention may be carried out in practice.

#### EXAMPLE.

Titanium tetrachloride is obtained by the chlorination, under reducing conditions, of titaniferous materials. The operation may be carried out so as to yield titanium chloride containing but relatively small amounts of impurities. The

titanium tetrachloride is then dissolved in two volumes of cold water yielding a clear aqueous chloride solution of titanium containing about 15 per cent. titanium dioxide. All the iron present is reduced to the ferrous condition by any one of the known methods, such as by the introduction of metallic zinc. In order to ensure the absence of ferric iron throughout the precipitation, it is preferred to reduce the solution to a content of two to three grams per litre of titanium oxide in the titanous state.

1000 pounds of the chloride solution containing 15 per cent. titanium dioxide is added to 10,000 pounds of boiling water containing 10 pounds of oxalic acid during about one hour the boiling being maintained throughout the addition. When the addition has been completed about 95 per cent. of the titanium will have been precipitated as hydrated titanium compounds in a coagulated form such that it settles well and may be readily filtered and washed. After filtration and washing the precipitate is converted to the anhydrous rutile form by calcining at a temperature of from 700 to 1000° C.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to be by my foreign correspondents, I declare that what I claim is:—

1. A process for the production of titanium dioxide having the rutile crystal-

line structure comprising hydrolysing an aqueous solution of titanium tetrachloride and calcining the precipitate wherein the hydrolytic precipitation is effected in the presence of negative divalent ions derived from a substance added to the solution in a proportion not exceeding 0.1 mol. to each mol. of titanium reckoned as  $TiO_2$  present in the hydrolysis solution, and wherein the hydrolytic precipitation is effected in the absence of any added insoluble material suspended in the solution.

2. A process as claimed in Claim 1 wherein an aqueous solution of titanium tetrachloride is added to hot water containing the negative divalent ion and the mixed solutions are heated to effect the hydrolysis precipitation.

3. A process as claimed in Claim 1 or 2 wherein sulphuric, tartaric or oxalic acid or one of their alkali metal salts is employed to provide the negative divalent ion.

4. A process for the production of pure titanium dioxide, having the rutile crystalline structure, as claimed in Claim 1 carried out substantially in the manner hereinbefore described in the specific example.

5. Pure titanium dioxide having the rutile crystalline structure when obtained by the process claimed in any of the preceding claims.

Dated this 18th day of September, 1936.  
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Chartered Patent Agents.